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Preparation of a Spherical Morphology of Tetranitroglycoluril (TNGU)

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ARL-TR-6940 **May 2014**

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14. ABSTRACT
A new, spherical morphology of tetranitroglycoluril (TNGU) has been prepared from the solvent, anti-solvent interaction of nitric acid and dichloromethane. This spherical morphology is significantly less sensitive to impact, friction, and static discharge than TNGU as isolated according to literature methods. The spheres averaged in size approximately 3 μ and appear to be uniform in size by scanning electron microscopy.

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1. Introduction

Tetranitroglycoluril* (TNGU) **1** is a high explosive that was first patented by the French in 1975 and then described in subsequent publications (*1–4*). This material has been measured to have a density of 2.01 g/milliliter (mL) and heat of formation (ΔH_f) of +50 kilo-Joules per mole (kJ/mol). The combination of these two properties make the predicted performance of **1** mimic that of the standard military explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, **2**) and 2,4,6,8,10,12-Hexanitro-2,4,6,8, 10,12-hexaazaisowurtzitane (CL-20, **3**) (*5*) (figure 1).

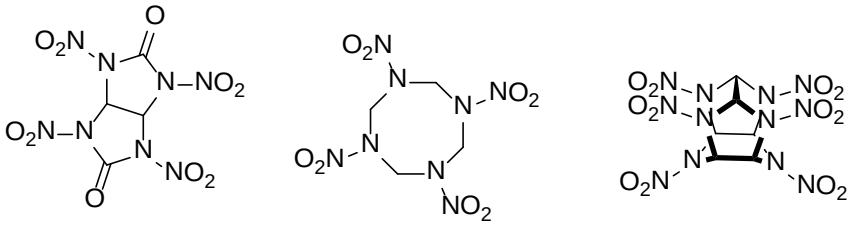


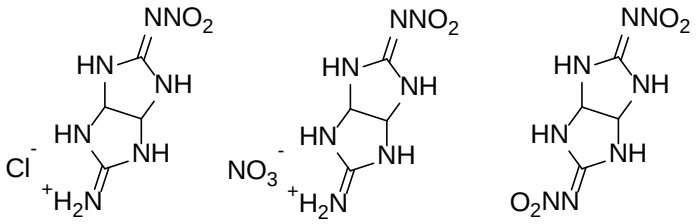
Figure 1. Structures of high explosives TNGU, HMX, and CL-20.

While **1** is a very powerful explosive, it has several disadvantages that have precluded its adoption as a standard military explosive. The first of these is its inherent instability in the presence of water. Due to the extreme electron deficiency of the carbonyl of the dinitrourea moiety, that center is incredibly susceptible to nucleophilic attack even by water through exposure to a moist atmosphere. The reactivity of this dinitrourea is unaffected through substitution at the bridgehead position (*6–7*). Unfortunately, this means the half-life of TNGU exposed to the atmosphere with a relative humidity approaching 85% can be on the order of days making it difficult to incorporate into formulations intended for standard military applications (*8*). While this feature may eliminate it from consideration for standard munition fills, it is potentially finding uses in self-remediating formulations specifically designed to have short environmental residence times after deployment and to lessen the hazards associated with unexploded ordinance (UXO) (*9*).

While the hydrolytic stability of **1** can potentially be exploited to form self-remediating munitions, the heightened sensitivity of the material to external insult is also detrimental to its incorporation into useful formulations (*8*). TNGU, as isolated using literature methods, has a 50% initiation (H_{50}) value for impact sensitivity of 4.09 inches (in) while 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and HMX are both close to 9 in. Additionally, TNGU has a friction

*Also known as Sorguyl.

measurement of 54 newtons (N) while RDX and HMX both are typically 120 N. Taken together, both of these numbers place TNGU in a category of material that is usually deemed too sensitive for secondary or booster applications. In a recent publication, it was disclosed that **1** prepared by the nitration of imidazo imidazoles **4**-**6** (figure 2) does have a markedly improved sensitivity over other methods of preparation (*10*) (also refer to table 2 in section 3).



4 **5** **6**

Figure 2. Structure of starting material imidazo imidazoles 4–6.

2. Morphological Studies

TNGU as obtained from the literature method is obtained as small clumps of fine needles that appear to have significant gaps in between the needles (figure 3). This needle like morphology is similar to what was reported in the literature (*10*). There are no other differences between the materials in the experimentally determined sensitivity, decomposition point, or chemical analysis.

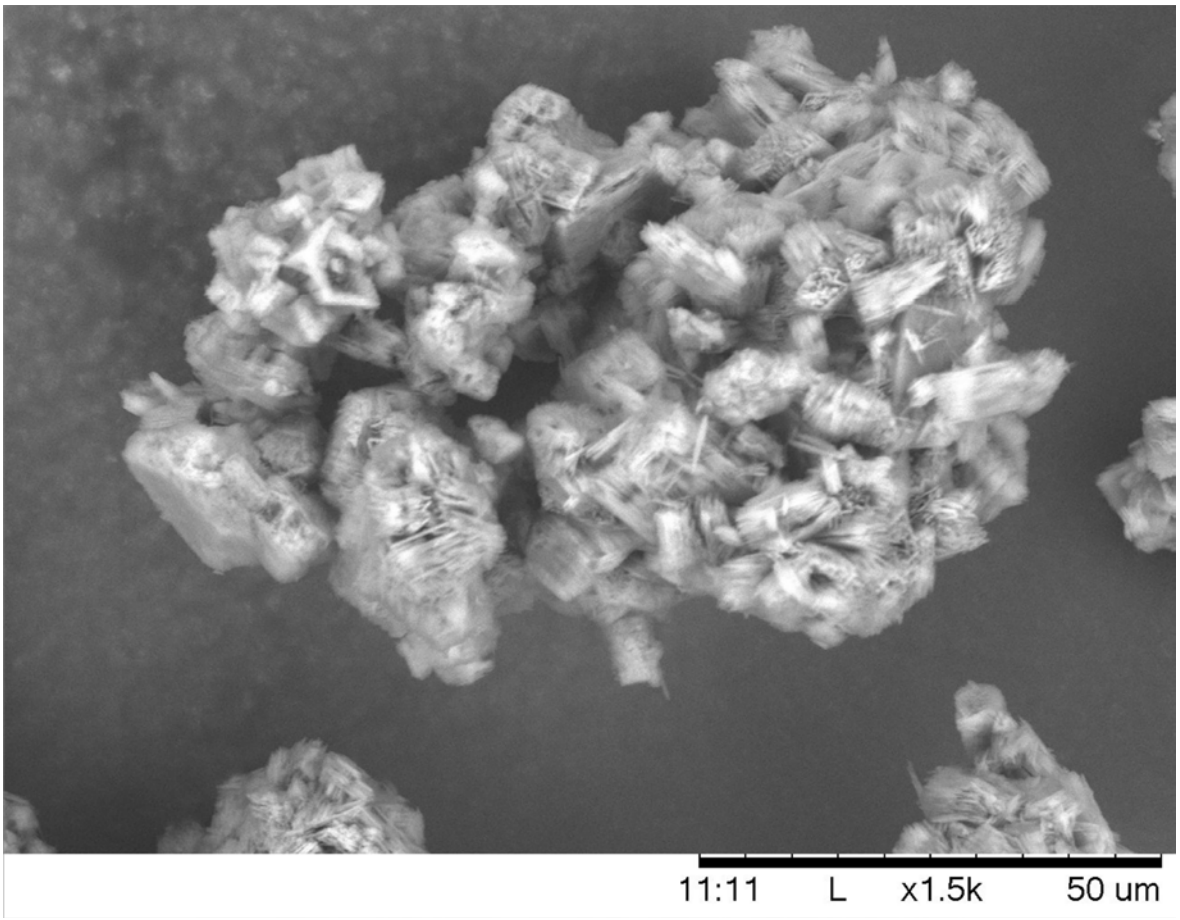


Figure 3. TNGU as isolated from literature method.

TNGU derived from the imidazo imidazoles **4-6** has a slightly different morphology than that obtained from the literature method (*9*) (figure 4). While it is still composed of needles, the needles are significantly longer and thicker than what is observed from the literature material. This slight difference in morphology could be partially responsible for the observed decrease in the sensitivity of the material obtained from the imidazo imidazoles (*10*).

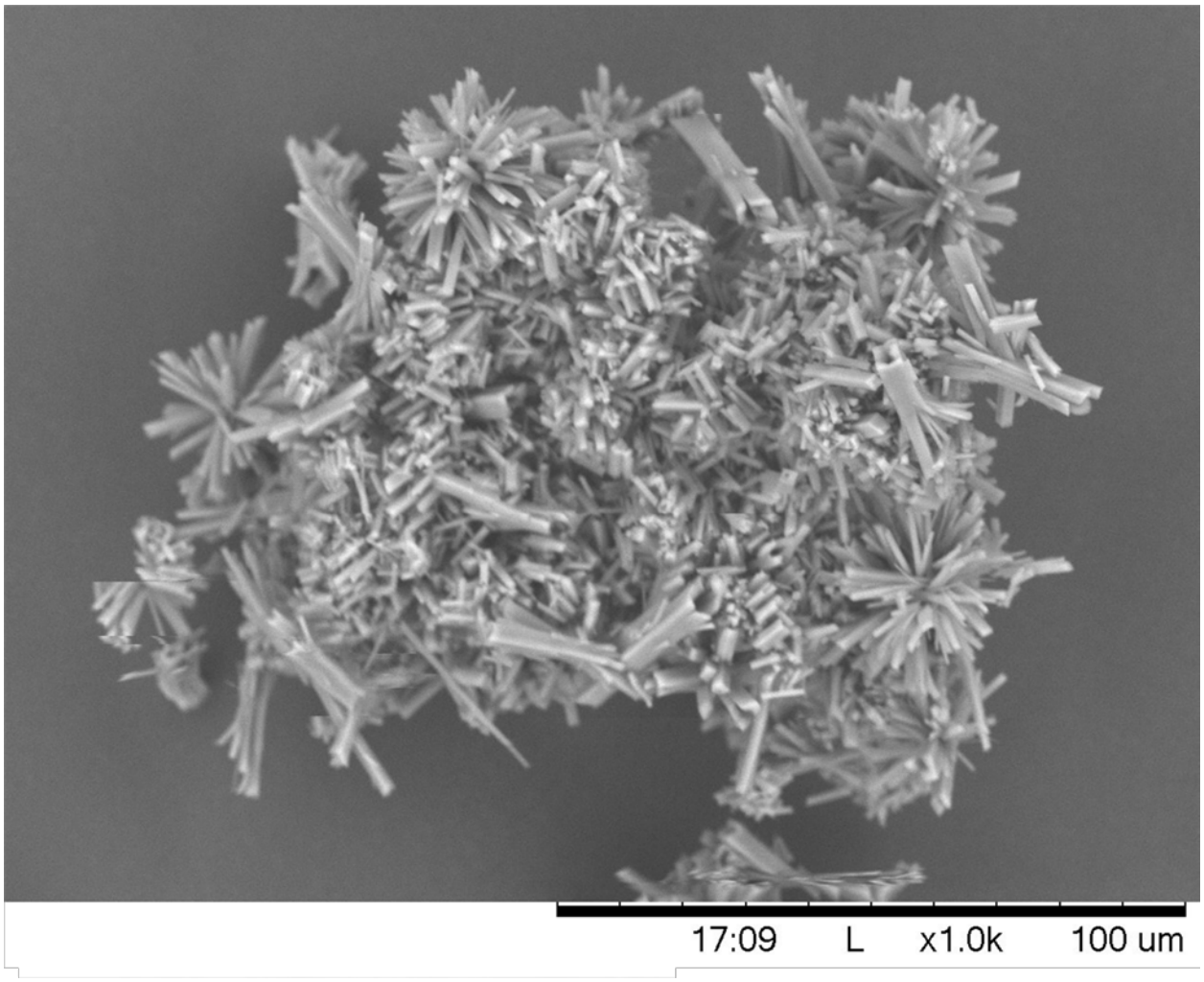


Figure 4. TNGU as isolated from imidazo imidazoles.

In examining various other morphologies of TNGU through recrystallization of the material, a spherical morphology exhibiting improved sensitivity over even the material synthesized from **4-6** was discovered (figure 5).

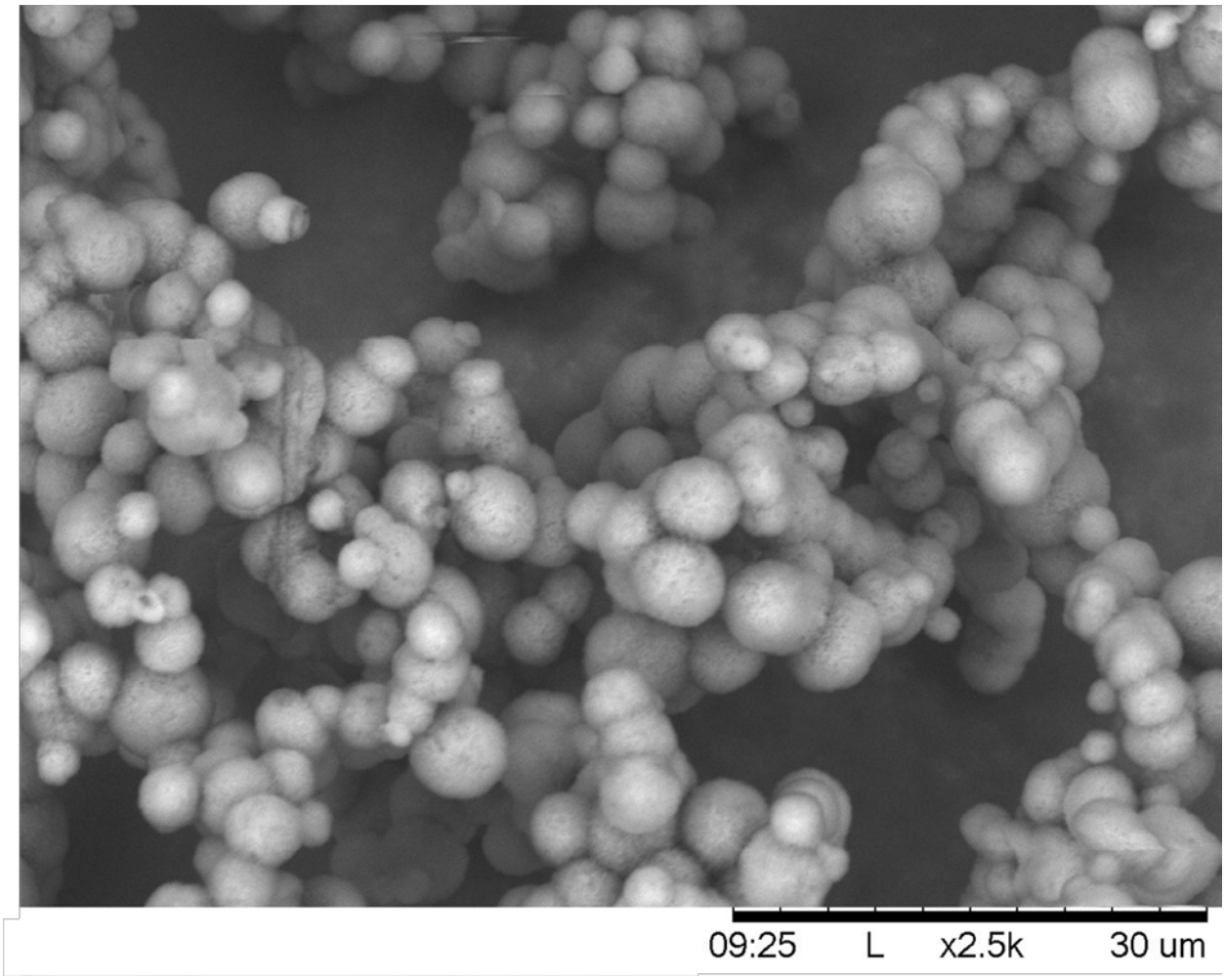


Figure 5. TNGU after sphericalization treatment.

While many other morphologies of TNGU have been reported, this appears to be the first time a spherical morphology of the material has been described. This morphology is easily obtained through solvent/anti-solvent interactions by first dissolving the material in 100% nitric acid (HNO_3) and precipitating it by introducing it below the surface of dichloromethane (DCM). The size and quality of the spheres appears to be determined by the rate of addition of the TNGU solution as well as the ratio of HNO_3 to DCM (table 1). It is worth noting, the only solvent system observed to generate spheres is 100% HNO_3, DCM. Using 90% HNO_3 or other solvents such as ethyl acetate, acetone, and acetonitrile with DCM as the anti-solvent does not result in the formation of spheres.

Table 1. Optimization of sphericalization procedure.

Scale (milligram [mg])	HNO_3 (mL)	DCM (mL)	Stir Rate (RPM)	Morphology
25	0.025	1	0	Cubes
25	0.025	10	0	Spheres and needles
25	0.025	10	500	Spheres
640	6.4	100	500	Spheres
2270	22.7	200	500	Spheres

3. Spherical Morphology Sensitivity Analysis

Sphericalized TNGU obtained from treating **1** prepared via the literature method and from **1** prepared from imidazo imidazoles was subjected to the standard suite of safety tests, impact, friction, and electrostatic discharge (ESD). It was found the material prepared from the literature method had an H_{50} drop height value of 13.07 in and material prepared from the imidazo imidazole had a drop height value of 15.39 in (table 2).

Table 2. Sensitivity analysis of various morphologies of TNGU.

Substance	Impact (in)[a]	Friction (N)[b]	ESD (Joules [J])[c]
1[d]	4.09	54	3.25
1[e]	11.06	70	3.25
1[f]	13.07	72	3.25
1[g]	15.39	94	3.25
HMX	9.61	120	0.025

[a]H_{50} impact height determined on an apparatus using a 5-lb weight by the Langlie one-shot method (*11*). [b]Friction determined on a Julius Peter's BAM friction apparatus. [c]ESD determined using an ABL Laboratories ESD apparatus. [e]**1** prepared according to literature procedure (*9*). [d]**1** prepared from **4**-**6** (*10*). [f]Sphericalized **1** that was synthesized according to literature procedure (*9*). [g]Sphericalized **1** that was synthesized from the nitrate salt 6 (*10*).

4. Conclusions

A spherical morphology of TNGU has been discovered which is more resistant to external insult than other, previously known morphologies. The material is obtained through the solvent/anti-solvent interaction of HNO_3 and DCM. While the new morphology does not rectify the hydrolytic instability of TNGU, it does greatly improve the sensitivity of the material making it safer to handle and investigate.

5. Experimental

H_{50} values for drop weight testing were determined using the Langlie one-shot method on a tester dropping a 5-lb weight from a maximum height of 60 in (*11*). Friction sensitivity measurements were determined on a BAM friction apparatus and ESD was determined using an Advanced BioScience Laboratories (ABL) ESD apparatus. Nuclear magnetic resonance (NMR) experiments were done using an Anasazi Instruments 90-megahertz (MHz) NMR. All chemicals were obtained from Sigma-Aldrich, St. Louis, MO and were used as received.

Note: While these compounds were prepared without incident according the following procedures, these materials are energetic and should be prepared and handled cautiously by trained personnel.

Preparation of TNGU according to the literature method (*9*)

To a round bottom flask cooled to 0 °C under a nitrogen (N_2) atmosphere was added 35 mL (54 g, 859 mmol) of 100% HNO_3. When the temperature of the acid was less than 5 °C, glycoluril (2 g, 14.1 mmol) was added slowly, portion-wise to keep the temperature of the solution less than 10 °C. Once all of the glycoluril was added and had dissolved, it was allowed to stir for 30 minutes (min) in the ice bath. A total of 18 mL (19.4 g, 190 mmol) of acetic anhydride (Ac_2O) was added drop-wise to the solution while keeping the temperature of the solution at less than 10 °C. (CAUTION: Highly exothermic.) Upon completion of the addition of the Ac_2O, the solution was removed from the ice bath and allowed to stir at ambient temperature for 4 hours (h). During this time a white precipitant of TNGU was observed forming in the solution. Once the 4 h had elapsed, the solution was filtered, and the filter cake was washed rapidly with ice cold water (50 mL), followed by a mixture of 50:50 chloroform/ethanol by volume (50 mL), followed by chloroform (50 mL). The material was then dried under vacuum (10 torr, 20 °C) for several hours and stored in a vacuum desiccator over Drierite*. The total amount of material recovered was 3.4 g (10.5 mmol, 74%).

Peak decomposition was observed to be 217–220 °C in the DSC. ^{1}H NMR (600.182 MHz, Acetone-D_6) δ 7.78 (s, 2H); ^{13}C NMR (150.046 MHz, Acetone-D_6) δ 141.8, 65.3; Fourier transform infrared (FTIR) (DATR),ñ =2997, 2894, 1798, 1652, 1617, 1594, 1255, 1144, 1090, 768, 730, 698; $C_4H_2N_4O_{10}$: calcd C 14.92; H 0.63; N 34.79%; found: C 14.89; H 0.63; N 34.72%.

*Drierite is a registered trademark of W.A. Hammond Drierite Co., Ltd.

Spericalization Procedure

A typical procedure at the 2-mmol scale: TNGU (640 mg, 2 mmol) is dissolved in 6.4 mL of ≥ 98% HNO_3 at 20–25 °C. This homogenous solution is then introduced below the surface to a stirring beaker of DCM containing approximately 100 mL a rate = 1 mL/min. Once the addition is completed, stirring is stopped, and the TNGU settles to the bottom of the beaker. The supernatant is decanted, the TNGU is resuspended in approximately 25 mL of DCM then allowed to settle. This washing procedure is repeated 4 to 6 times until no HNO_3 remains. The TNGU is then vacuum dried to remove the residual DCM and stored in a desiccator over Drierite. The amount of spherical TNGU recovered from this process is 462 mg (1.43 mmol, 72%). Scanning electron microscopy of the material from this process stirring at a rate of 250 revolutions per minute (RPM) yields spheres approximately 3 µ in diameter.

A typical procedure at the 7-mmol scale: TNGU (2.27 g, 7 mmol) is dissolved in 22.7 mL of ≥ 98% HNO_3 at 20–25 °C. This homogenous solution is then introduced below the surface to a stirring beaker of DCM containing approximately 200 mL at a rate of = 1 mL/min. Once addition is completed, stirring is stopped, and the TNGU settles to the bottom of the beaker. The supernatant is decanted, the TNGU is resuspended in approximately 50 mL of DCM then allowed to settle. This washing procedure is repeated 4 to 6 times until no HNO_3 remains. The TNGU is then vacuum dried to remove the residual DCM and stored in a desiccator over Drierite. The amount of spherical TNGU recovered from this process is 1.66 g (5.15 mmol, 73%). Scanning electron microscopy of the material from this process stirring at a rate of 250 RPM yields spheres approximately 3 µ in diameter.

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List of Symbols, Abbreviations, and Acronyms

ΔH_f	heat of formation
ABL	Advanced BioScience Laboratories
Ac_2O	acetic anhydride
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8, 10,12-hexaazaisowurtzitane
DCM	dichloromethane
ESD	electrostatic discharge
h	hour
H_{50}	50% initiation height
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HNO_3	nitric acid
in	inches
J	Joules
kJ	kilo-Joules
mg	milligram
mL	milliliter
MHz	megahertz
min	minute
mol	mole
N	newton
N_2	nitrogen
NMR	nuclear magnetic resonance
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
RPM	revolutions per minute
TNGU	tetranitroglycoluril
UXO	unexploded ordinance

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